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Calculation of the Work of Adhesion of Solid-Liquid Interfaces by Molecular Dynamics Simulations

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Colloids, polymer-nanocomposites or polymers and liquids in contact with extended surfaces are examples of systems in which interfaces play a crucial role. The stability of such materials is dominated by the thermodynamic properties of these interfaces. Further advances in the development of those materials require a better understanding of the connection between the interfacial intermolecular interactions and these thermodynamic properties. In our project, we develop algorithms to quantify thermodynamic quantities at the solid-liquid interface through molecular dynamics simulations and relate them to the intermolecular interactions and to the interfacial structure of the liquids. We illustrate our approach through the example of the water-graphene system which has intensively been discussed in the last few years. We also discuss the perspectives our approach opens in multiscale modelling of interfacial soft-matter systems.

1 Introduction

Adhesion of paint on a metal surface, the roll-off motion of a water drop on a plant leaf or liquid flow on a chip for medical applications are typical examples of phenomena where the interaction between a polymer or a liquid and a surface plays a crucial role. The stability and the thermal, mechanical, optical or electrical properties of materials such as colloidal suspensions, nanofluids or polymer nanocomposites to mention a few also strongly depend on the intermolecular interactions at the interface between a liquid or a polymer matrix and solid particles. While experiments to probe structures on distances of a few angstroms in the vicinity of solid surfaces and relate the corresponding observations to thermodynamic information require further development, classical molecular dynamics (MD) simulations and quantum calculations are methods of choice to characterise interfaces at the molecular scale. These approaches show that liquids and polymers adopt a layer structure in the vicinity of surfaces whose magnitude depends on the strength of the interaction. This is illustrated in Fig. 1 where we compare the mass distribution of water on a gold surface and on a graphene monolayer as obtained by MD simulations.

Through the combination of statistical thermodynamics and MD simulations performed on JUROPA and now on JURECA we address the question of how such a peculiar interfacial structure influences the wetting and adhesion properties of liquids and polymers on surfaces. The principles of the methodologies we have developed to reach this goal are briefly discussed. We illustrate how they have been employed to contribute to understand better the wetting properties of graphene. In fact, this research topic of considerable importance has strongly benefited from molecular simulations carried out by several groups to understand experiments.

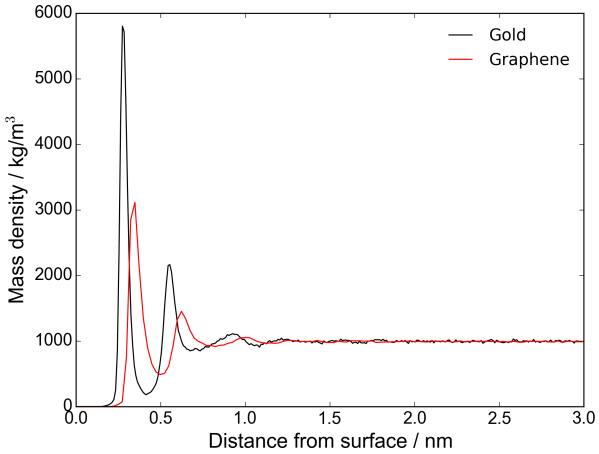

Figure 1. Mass density distribution of water perpendicular to the (111) gold surface (black line) and to a single layer of carbon atoms (graphene monolayer, red line). The results were obtained by classical MD simulations using the interaction parameters of Ref. 1 and 2, respectively. Note that a similar structure of water on graphene was recently obtained through *ab initio* calculations[3].

2 Algorithms to Calculate Solid-Liquid Work of Adhesion

In this section we define the solid-liquid work of adhesion and present two algorithms derived by us to calculate it. The solid-liquid work of adhesion W_{SL} is defined as the reversible work to separate a solid and a liquid initially at contact and to bring them at a distance where they no longer interact. It is expressed in terms of surface and interfacial tensions following:

$$W_{SL} = \gamma_S + \gamma_L - \gamma_{SL} \tag{1}$$

where γ_S is the solid surface tension and γ_L is the liquid surface tension, whereas γ_{SL} is the solid-liquid interfacial tension. In Eq. 1, it is assumed that liquid has a vapour pressure low enough such that the excess amount of vapour adsorbed on the surface is negligible[4]. Moreover, solids are considered to be stiff enough, such that there is negligible plastic deformation of the surface upon separating solid and liquid. Under these conditions, the solid-liquid interfacial tension (force per unit distance) is equal to the solid-liquid interfacial excess free energy (energy per unit area). We are interested in fluids with low vapour pressure such as water at ambient condition and ionic liquids as well as polymers on substrates like gold or graphitic surfaces. Therefore, those conditions are met in the study of the systems we aim to consider. Since W_{SL} is defined as the free energy change per unit area, it may be accessed through free energy calculations, as discussed in more detail below. Such calculations represent a central question in the characterisation of the thermodynamic properties of liquid and of soft matter systems. They have thus benefited from numerous methodological studies and are well established.

The thermodynamic quantities that define W_{SL} also control the shape of a droplet of a given liquid on a given surface. This shape is measured through the contact angle θ which

relates to W_{SL} through the equation of Young-Dupré below:

$$W_{SL} = \gamma_L(1 + \cos\theta) \tag{2}$$

Eq. 1 and Eq. 2 suggest several numerical approaches that may be employed to quantify W_{SL}. A first possible approach consists in determining γ_{SL}, γ_L and γ_S independently and combine them following Eq. 1. The calculation of γ_L has benefited from several methodological developments[5], and the estimation of γ_S for stiff and ordered materials is in principle accessible provided that a model to describe the interactions within the solid exist. In contrast much fewer methodologies lead to the determination of γ_{SL}. γ_L is often determined through the spatial integration of the stress tensor anisotropy[5]. This method proves very demanding in terms of computation time for realistic systems. Due to their mathematical nature (second order quantities), the pressure tensor components are characterised by slow convergence, such that several tens or hundreds of nanoseconds are generally required to determine γ_L with statistical uncertainty less than 10 % for polymers or fluids with electrostatic interactions. γ_{SL} may also be determined through the stress tensor analysis mentioned above with the same slow convergence. Alternatively, one may determine γ_L on the one hand, and θ through the simulation of droplets on the other hand, finally to combine them following Eq. 2. However, θ may be affected by size effects in a way that remains poorly understood (see Ref. 1 and references therein). In fact, the dependence of θ on the droplet size is still an open question in surface science[6].

Rather than calculating interfacial tensions separately and combining them in Eq. 1, we determine W_{SL} directly. We treat this quantity as a free energy change per unit area, and determine it following the formalism of the well established thermodynamic integration approach[7]. This approach leads to faster convergence, such that computation time can be employed to sample extensively the parameter space and gain detailed knowledge that would not be accessible otherwise. In this context, we derived two methods that will be detailed below. These two methods are based on a common observation about the behaviour of water on repulsive surfaces. MD simulations showed that water tends to avoid such surfaces and forms a liquid-vapour like interface in their vicinity. This result had already been obtained in the case of water in contact with spherical repulsive particles whose radius is larger than a few nanometres[8]. We found that it also applies to planar surfaces[1] and exploited it to derive two algorithms, namely the phantom-wall methodology[9] (Sec. 2.1) and the dry-surface method[1] (Sec. 2.2). In these two approaches, the interface of interest is turned into an effectively repulsive interface. As mentioned above, thermodynamic integration is employed to calculate the Gibbs free energy change ΔG upon turning the actual interface into the effectively repulsive one. This approach can be understood from the following generic formula:

$$\Delta G = \int_{\lambda_A}^{\lambda_B} \left\langle \frac{\partial \mathcal{U}_{SL}}{\partial \lambda} \right\rangle \mathrm{d}\lambda \tag{3}$$

where λ is a parameter that quantifies the reversible path along which the transformation from the actual interface (λ_A) to the repulsive interface (λ_B) is carried out. $\mathcal{U}_{SL}$ is the total solid-liquid interaction energy and the brackets denote an average in an appropriate statistical ensemble. Eq. 3 shows the connection between ΔG which is directly proportional to the macroscopic quantity W_{SL} and the microscopic quantity $\mathcal{U}_{SL}$ which directly depends on the solid-liquid intermolecular interactions. Both the phantom-wall and the dry-surface

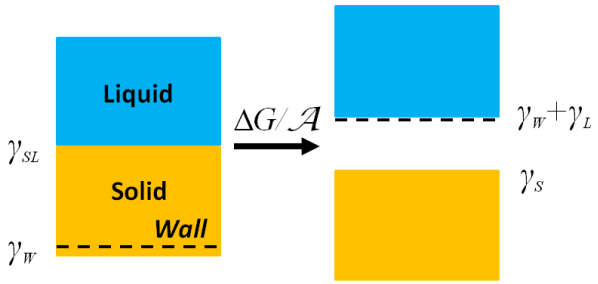

Figure 2. Principle of the phantom-wall method to obtain the solid-liquid work of adhesion. Only the initial step where liquid only interacts with solid and the final step where liquid only interacts with the phantom wall are represented.

methods are implemented in such a way that the free energy change per unit area of this process is equal to $\gamma_S + \gamma_L - \gamma_{SL}$, i.e. the quantity that defines W_{SL} (Eq. 1).

2.1 The Phantom-Wall Algorithm

In the phantom-wall approach[9], the solid-liquid interface of interest is turned into a repulsive interface by the action of a wall. This wall is initially present within the solid surface (see Fig. 2), but has no interaction with liquid. The wall is then reversibly shifted perpendicular to the surface such that it interacts with liquid. At the end of the process, the wall is located at a distance such that the liquid only interacts with it and no longer with the solid. The Gibbs free energy change per unit area associated with the transformation described above is:

$$\frac{\Delta G}{\mathcal{A}} = \gamma_S + \gamma_L - \gamma_{SL} + P_N \Delta V \tag{4}$$

where $\mathcal{A}$ is the cross-sectional area of the interface, P_N is the pressure component perpendicular to the surface and ΔV is the volume change of the system that arises from the wall's displacement. The direct outputs of MD simulations are ΔG and $P_N \Delta V$, whose determination directly leads to W_{SL}.

The phantom-wall approach proved to be particularly adapted for the study of rough surfaces[10,11], as will be demonstrated in a concrete example below.

2.2 The Dry-Surface Approach

Following the dry-surface approach[1], a given solid-liquid interface of interest is turned into an effective repulsive interface. This is realised by turning the actual interfacial interaction potential into an effectively repulsive potential, while maintaining the solid-solid and liquid-liquid interactions unchanged. Similarly to the phantom-wall approach, water avoids the surface as it is turned repulsive. Consequently, the free energy change per unit area associated with this process is equal to $\gamma_S + \gamma_L - \gamma_{SL}$, which is the quantity that defines W_{SL} (see Eq. 1).

The dry-surface method is well adapted to smooth interfaces and may be used to optimise force-field parameters based on experimental quantities such as contact angles, as will be discussed below. It represents a valuable tool to rapidly sample the parameter space. We have recently generalised its application to fluids other than water and to coarse-grained models in which select degrees of freedom are removed[12], such that phenomena occurring at time and length scales larger than accessible through atomistic simulations may be studied. We briefly discuss this extension in Sec. 4.

3 The Interaction between Water and Graphene

The question of the strength of the interaction between a given compound and graphene is of crucial importance in materials where graphene flakes or even carbon nanotubes are embedded in a polymer matrix or dispersed in a fluid, as well as when graphene is used to coat a surface and is in direct contact with liquid droplets. In a series of experimental works supported by MD simulations, measurements of the contact angle of water droplets on graphene layers adsorbed on various substrates were performed[13–15]. It was found that coating a substrate may have different effect on the wetting behaviour of the coated surface. The contact angle on hydrophilic surfaces like gold is almost not affected by the presence of graphene[13]. In contrast, the contact angle on coated hydrophobic surfaces was found to be influenced by the presence of graphene[14]. Hydrophilic surfaces which form hydrogen bonds with water are turned into much less hydrophilic substrates when coated with graphene[13]. In fact, the presence of graphene prevents the possibility to form hydrogen bonds between water and the underlying substrate, interactions which are at the origin of the strong interaction between water and the hydrophilic bare substrate.

The experiments mentioned above were conducted with surfaces coated with graphene, such that inferring the intrinsic wetting behaviour of graphene is not straightforward. In this context we performed MD simulations of water on isolated graphene surfaces, i.e. with no substrate, and calculated W_{SL} through phantom-wall calculations depending on the number of graphene layers[16]. We showed that and explained why the contact angle of water on a single graphene layer differs from its value on graphite (quasi-infinite stack of graphene layers) only by a few degrees. Our conclusion was confirmed by experiments on super-hydrophobic surfaces[14]. We found that the interaction between water and graphene is short-ranged, such that the interaction with the first carbon layer of graphite dominates. The second and third layers have a weaker influence, and layers beyond the third one play a negligible role. Thus, if one removes all carbon layers but the last one of a stack, the interaction between water and the surface is only weakly modified. At the macroscopic scale, a small increase in the contact angle would be observed when turning graphite into mono-layer graphene[16].

Further experiments have shown that the contact angle of water on graphite surfaces is very sensitive to the adsorption of volatile organic compounds[17,18]. These compounds are hydrophobic molecules like short alkanes and alkenes which make the substrates on which they adsorb appear effectively more hydrophobic than they are. MD simulations have confirmed that the adsorption of alkanes on graphite increases the contact angle of water drops, but no molecular mechanism has been proposed[18]. In a work performed on JUROPA, we studied the effect of superficial roughness on the work of adhesion of water on graphite through phantom-wall calculations[10]. We employed graphite model surfaces

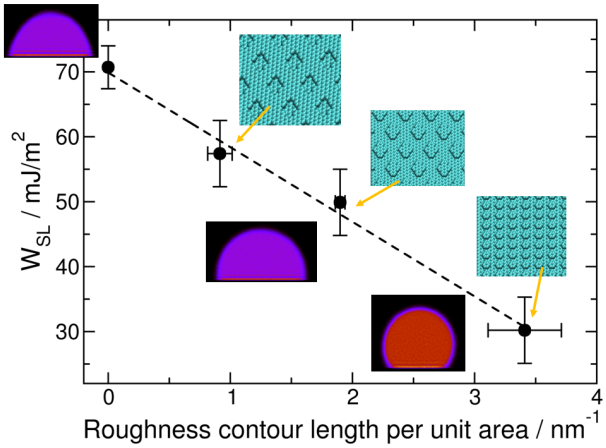

Figure 3. Work of adhesion for water on graphite with superficial defects of various contour length. The defect patterns are represented on the plot next to the respective value of W_{SL} they yield. Additionally, the shape that a nanometre sized droplet takes on these surfaces is represented in purple and red. As expected from Eq. 2, the contact angle increases when W_{SL} decreases, i.e. when graphite becomes more hydrophobic.

where atoms of the top layer were selectively removed to form specific patterns whose contour length was varied (see Fig. 3). Surfaces with such superficial defects can serve as model surfaces to study the effect of the adsorption of hydrocarbons on the wetting behaviour of a surface. Indeed, alkane molecules have interaction with water which is close to the interaction between water and graphitic carbon atoms. Moreover, surface defects may be seen as isolated molecules or small clusters of molecules adsorbed on the surface. Similarly to the effect of alkane adsorption, we found that the work of adhesion of water on rough surfaces decreases compared with smooth defect-free surfaces. In other words, the surface becomes more hydrophobic, when superficial roughness is implemented. We also showed (as illustrated in Fig. 3) that W_{SL} is proportional to the contour length per unit area of the defects. This behaviour was explained by the fact that the upper corners of the defects represent high energy sites for water due the missing carbon atoms. In order to minimise the perturbation of its hydrogen-bonding network induced by the presence of the surface, water is forced to experience these high energy sites, and the energy of the system increases along these defect corners[10]. Hence the linear decrease of W_{SL} reported in Fig. 3. It can thus be observed that molecular simulations represent a valuable tool to both confirm experimental trends and propose models to interpret them. In this regard, it is interesting to note that all the experimental works reported above were published with MD simulation results.

The fact that adsorbed volatile organic compounds have a non-negligible effect on the contact angle of water on graphite implies that the intrinsic interaction between water and graphitic surfaces is stronger that previously thought[17,18]. Precise contact angle measurements are of crucial importance because this macroscopic quantity may be used to optimise classical force-field parameters. For example, MD simulations of nanometre sized droplets were used to parameterise the water-carbon interaction used in numerous sim-

ulation works[19]. Quantum calculations may also be employed to obtain parameters for classical force-fields[2]. It is important to note that contact angle and work of adhesion depend on liquid-liquid, solid-solid but also on solid-liquid interactions. Thus these quantities are observables which inherently depend on the collective behaviour of water molecules. There is *a priori* no direct connection between the single water molecule energies delivered by quantum calculations and the macroscopic contact angle and W_{SL} values measured in experiments. Dry-surface calculations of W_{SL} performed in our group on JUROPA have achieved an important step towards this missing link[19]. We show how to connect W_{SL} obtained from experiments and MD simulations to the binding energy of water molecules on graphene surfaces obtained by quantum calculations.

4 Concluding Remarks

We have presented and discussed the capabilities of two methodologies derived by us to calculate the solid-liquid work of adhesion. This quantity characterises the thermodynamics of solid-liquid interfaces which play a major role in systems whose behaviour is dominated by such interfaces. Results concerning the interface between water and graphene layers were presented. The dry-surface method was recently extended to coarse-grained (CG) models. In such models, the number of atoms is reduced such that phenomena like the assembly of nanoparticles occurring at a more mesoscopic scale can be tackled. When the number of degrees of freedom of a given system is decreased, its potential energy surface is also affected. We then addressed the question of how the interfacial thermodynamics is modified by the process of coarse-graining, a topic where little progress has been reported so far. We are interested in CG models which retain the chemical reality of the system of interest, i.e. models beyond generic behaviour. As a first step, we characterised the work of adhesion of n-hexane on graphene layers and formulated general recommendations on how to design CG potentials to preserve the value of W_{SL} upon coarse-graining. This work is expected to enhance the understanding of CG potentials for heterogeneous interfacial systems, systems we will address in future works.

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